

Impacts of freezing and thermal treatments on dimensional and mechanical properties of wood flour-HDPE composite

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Abstract: Wood plastic composite (WPC) of wood flour (WF), high density polyethylene (HDPE), maleic anhydride-grafted polyethylene (MAPE) and lubricant was prepared by extrusion, and then exposed to different temperatures to evaluate the effects of freezing and thermal treatment on its dimensional and mechanical properties. At elevated temperatures, WPC expanded rapidly initially, and then contracted slowly until reaching an equilibrium state. Treatment at 52°C and relative humidity of 50% for 16 days improved the mechanical properties of WPC: flexure, tensile strength, and izod unnotched impact strength increased by 8%, 10% and 15%, respectively. Wide-angle X-ray diffraction (XRD) tests showed that the degree of crystallization of HDPE in WPC declined with increasing treatment temperature.

Keywords: wood plastic composite; freezing treatment; thermal treatment; dimension; mechanical properties; X-ray diffraction

Introduction

WPCs are emerging as an important material in construction and attract interest because of their performance (Lee and Dae 2009; Adhikary et al. 2010). Recent advances in processing technology have improved WPC properties and thus increased their share of industrial markets (Smith and Wolcott 2006). WPCs have been used in increasingly widespread applications, especially in con-

struction of buildings and infrastructure, manufacture of automobiles, packing industries for military, and electronic and aerospace technology (Ou et al. 2010; Alireza 2008; Jiang et al. 2010). However, two characteristics of WPC boards, thermal expansion and shrinkage, limit their utility for designers (Anatole 2007). The performance of HDPE and HDPE-based composites are strongly dependent on the processing time and temperature of manufacturing (Sain et al. 2000). Yang et al. (2005) showed that the thermal stability of polymer bio-composites decreases slightly as the loading of lignocellulosic filler increases. WPCs undergo thermal expansion when manufactured at high temperatures and then shrink when used in subsequent applications (Alireza 2010). Little attention has been paid, however, to the effects of freezing and thermal treatment on the dimensional stability of WF-HDPE composites.

A study of polypropylene-pine WPC showed that loading of tension and compression decreased linearly with increasing temperature. Tension loadings that yielded maximum specimen strain increased appreciably with temperature, whereas a nearly constant maximum strain was determined for compression regardless of temperature (Schildmeyer 2006). Several researchers studied the effects of accelerated freeze-thaw cycles and freezing conditions on the mechanical properties of WPC, concluding that greater wood-flour content resulted in greater dimensional change and caused apparently deleterious effects on the strength of composites because of poor interfacial adhesion (Jeanette and Laurent 2005; Jeanette and Laurent 2006). A large portion of the mechanical property loss was associated with moisture absorption rather than the freeze-thaw cycle (Pilarski and Matuana 2006) and the size of the specimens strongly affected the mechanical strength of composites (Wang and Morrell 2005). Processing at higher temperatures is a selectable way to relax potential processing stresses in WPC (Andrew et al. 2009) and effectively protect the composites from generating cracks. Studies of wood fiber processed using a thermal treatment method that significantly improved the dimensional stability of WPC panels showed that flexural properties and inner bond stress are seriously affected by thermal treatment (Nadir 2011). Suitable environmental conditions such as 20°C and 65% humidity can help

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to maintain the mechanical properties of composites for long-term storage (Follrich et al. 2010).

We studied the dimensional changes and mechanical properties over time of WPC treated at different temperatures. We analyzed crystallization of WPC using wide-angle X-ray diffraction (XRD) (Han et al. 2008; Hung and Wu 2010).

Materials and methods

Materials

We analysed a WPC formulation (percent by weight) composed of 58% WF, 36% HDPE, 4% MAPE and 2% lubricant. WPC components were: HDPE (5000S resin, density $0.954 \text{ g}\cdot\text{cm}^{-3}$, melt flow index $0.9 \text{ g}/10 \text{ min}$, Daqing Petrochemical Co., China), wood-flour (WF) (20–40 mesh, Harbin Yongxu, China), maleated anhydride-grafted polyethylene (MAPE) (MA grafting ratio of about 0.9 wt% and melt flow index $2 \text{ g}/10 \text{ min}$ at 190°C , Shanghai Sunny New Technology Development Co., Ltd., China) and PE-wax (Brand Taiao, China).

Compounding and Processing

WF was dried at 105°C for 24 h. The WF, HDPE, MAPE and PE-wax were mixed in a high-speed mixer (10 min), and subsequently transferred to a twin-screw/single-screw WPC-one-step extruder system (model: BHMS-40/75 WPC extruder, Nanjing Xawax Science Technology Co., Ltd., China.) to directly produce WPC sheets ($4 \text{ mm}\times 60 \text{ mm}$) directly. The processing temperatures for extrusion were set at 155°C in the melting zone, 150 – 165°C in the pumping zone, and 165°C in the die zone. The rotation speeds of the feeding, twin-screw and single-screw were 60, 120 and 70 rpm, respectively.

The WPC sheets were then conditioned at $23\pm 2^\circ\text{C}$ and relative humidity (RH) of $50\%\pm 5\%$ for 6 months according to ASTM D618-99. Three WPC specimens ($4 \text{ mm}\times 60 \text{ mm}\times 140 \text{ mm}$) were then treated at -20 , 20, 52 and 80°C .

Determination of linear expansion and contraction coefficient k

According to ASTM D 6341, specimen size was measured using a vernier caliper at the interval of 12 h (total: 32 intervals) at the same position and pressure. Linear coefficient (k) of thermal expansion and contraction were determined.

Mechanical properties

Three-point bending tests were carried out with a universal mechanical machine (Shenzhen Regear Instrument Cooperation, China) at a crosshead speed of $2.0 \text{ mm}\cdot\text{min}^{-1}$ and span length of 64 mm in accordance with ASTM D790-2004, and the sample size was $80 \text{ mm}\times 13.7 \text{ mm}\times 4 \text{ mm}$. The dog-bone tensile specimens ($165 \text{ mm}\times 13 \text{ mm}\times 4 \text{ mm}$) were measured according to ASTM D638-2004. Crosshead speed of $5 \text{ mm}\cdot\text{min}^{-1}$ and gage length of 50 mm were used for the test. Izod unnotched impact

strength ($80 \text{ mm}\times 10 \text{ mm}\times 4 \text{ mm}$) was quantified using a JJ-20 impact tester (Changchun Intelligent Instrument & Equipment Co., Ltd., China) according to the ASTM D4812-2004 standard. At least five replicates of each treated WPC were tested and all the measurements were performed at 20°C and 50% RH.

X-ray diffraction (XRD)

Wide-angle X-ray diffraction (XRD) analysis was carried out with a MiniFlex diffractometer (Rigaku, Tokyo, Japan). XRD WPC samples were mounted to the XRD platform for analysis. A 2θ range from 5 to 35° in reflection mode was scanned at $2^\circ\text{C}\cdot\text{min}^{-1}$ at 40 kV and 30 mA. We used a computer-controlled wide angle goniometer coupled to a sealed-tube source of nickel filtered $\text{CuK}\alpha$ radiation ($\lambda = 15.4056 \text{ nm}$). Based on Scherrer's equation, in the long period, the crystalline thickness perpendicular to the reflection plane (L_{hkl}) of HDPE, was calculated as:

$$L_{hkl} = \frac{K\lambda}{\beta_0 \cos \theta} \quad (1)$$

Where, θ is half of the angle of diffraction; λ (0.154 nm) is the wavelength of the X-ray; β_0 is the width of the diffraction beam (rad); K is the shape factor of crystalline thickness, related to β_0 and, when β_0 is defined as the half-height width of diffraction peaks, $K = 0.9$. The crystallization peaks were treated using a multipeak separation program MDI Jade 5.0 to separate the amorphous peaks (Han et al. 2008).

Results and discussion

Linear expansion and contraction coefficient k

Virgin HDPE and WPC specimens were treated at -20°C , 20°C , 52°C and 80°C , and the change in sample length direction is shown in Fig. 1. The change at 20°C was near 0, therefore, the data are not shown in Fig. 1.

Treating temperature and time had a dramatic influence on the size of HDPE and WPC. HDPE exhibited a change of -0.59% , 0.34% , and 0.47% , respectively, with increasing temperature (Fig. 1A). WPC expanded at treating temperatures $>20^\circ\text{C}$ and shrunk at temperatures $<20^\circ\text{C}$. At -20°C , the length change ratio of specimens reached the peak value of -0.20% after treating for 24 h at constant temperature (linear contraction coefficient $k = -4.7 \times 10^{-5}$). At elevated temperatures (52°C and 80°C), the rate of change was more rapid than at low temperature, and the peak values ($+0.12\%$ and $+0.22\%$) were recorded after about 12 h. However, with prolonged treating time, the change ratio values gradually decreased and plateaued (linear expansion coefficient $k = 1.7 \times 10^{-5}$) after 16 days. The final length change ratios declined by 53% and 58%, respectively, compared with the maximum values. This phenomenon could be related to two factors, the adding of WF and other additives, and gradual release of potential processing stresses in WPC (Andrew et al. 2009) derived from the reconfiguration of HDPE molecules.

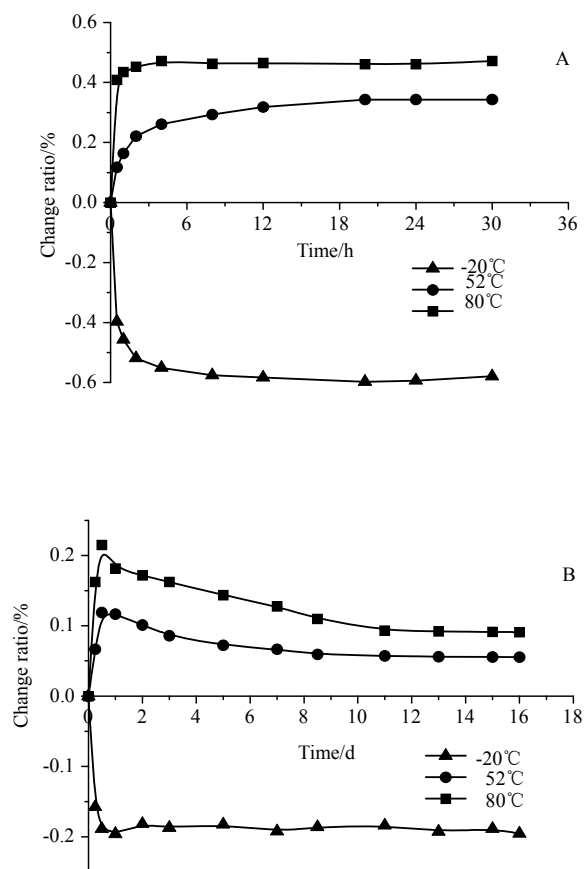


Fig. 1 Graph of length change rate over time of HDPE (A) and WPC (B)

Weight loss

Temperature dramatically affects weight loss of WPC composites: higher treating temperatures result in more rapid weight loss ratios. The weight loss ratios of specimens treated for 16 d reached 1.6% and 0.82% when treated at 80°C and 52°C, respectively.

Linear coefficients of thermal expansion-contraction for wood are significantly lower than for plastics and WPCs. The values for wood are independent of temperature between -51°C and 130°C (Simpson and TenWolde 1999). Because HDPE is a continuous phase in WPC, linear expansion and contraction are related to polymer molecules. When treated at elevated temperatures, polymer molecules begin to move and steadily reach their thermodynamically “settled state,” resulting in composite expansion (Anatole 2007). This, in addition to absorption of water, is another reason that WPC products expand. With prolonged treating time, WPCs gradually contract, which may be related to loss of weight, because when the change of weight is at a steady state, WPC specimen length is constant (Fig. 1B and Fig. 2). The substances lost from WPC are mainly low molecular weight materi-

als (LMWM) such as water vapor and lubricant. The potential processing stress readily concentrates at the wood fiber ends. The addition of additives such as lubricants and MAPE will contribute reducing stress. According to the time-temperature superposition principle, a rapid reorientation of the polymer chains at elevated temperatures under an applied constant stress which is equivalent to a slow reorientation of the polymer chains at lower temperatures for a longer time (Aklonis and MacKnight 1983). Elevated temperatures promote the release of potential stress at shorter times and induce the WPC contraction (Fig. 3).

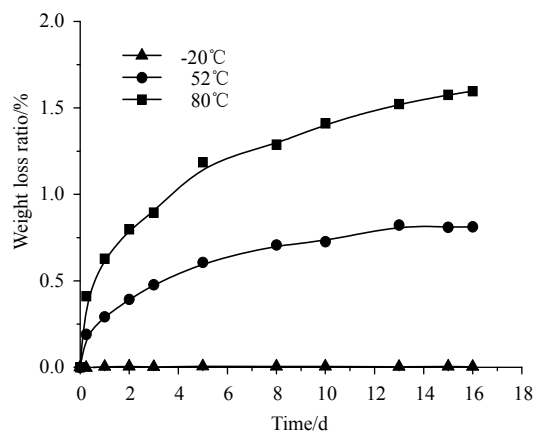


Fig. 2 Graph of weight loss change ratio of treated WPC over time

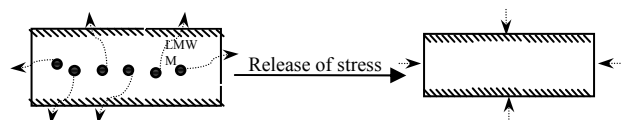


Fig. 3 The postulated scheme of 2-dimensional structure of WPC when releasing stress

Mechanical performance

Freezing and thermal treatment improved flexure strength by 8% but reduced the flexure modulus of WPC (Fig. 4). Treatment at 52°C resulted in an increase in tensile strength and a reduction of Young's modulus by 10% (Fig. 5). Fig. 6 shows Izod unnotched impact strength test results for treated and untreated samples: specimens treated at -20°C and 52°C showed increases of 15% and 6%, respectively. Thermal treatment can enhance molecule motion of polymer segments (Amash and Zugenmaier 1997), and might affect the mechanical behavior of composites by molecular rearrangement (Andrew et al. 2009). Within given ranges of processing temperature range and treatment duration, the mechanical properties of WPC can be improved, and this improvement might be attributed to the variation of degree of crystallization (Magnus and Kristiina 2006; Magnus and Kristiina 2006) due to the freezing or thermal treatment. Flexure and tensile modulus declined with reduced polymer crystallinity (Sperling 2006). Through the analysis above, we conclude that the thermal

treatment at 52°C for 16 days was beneficial to the mechanical properties of WPC.

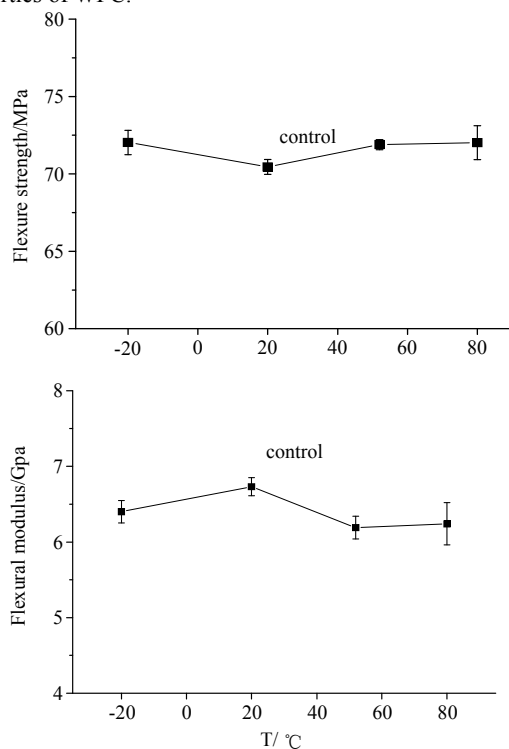


Fig. 4 Flexural properties of treated WPC by temperature

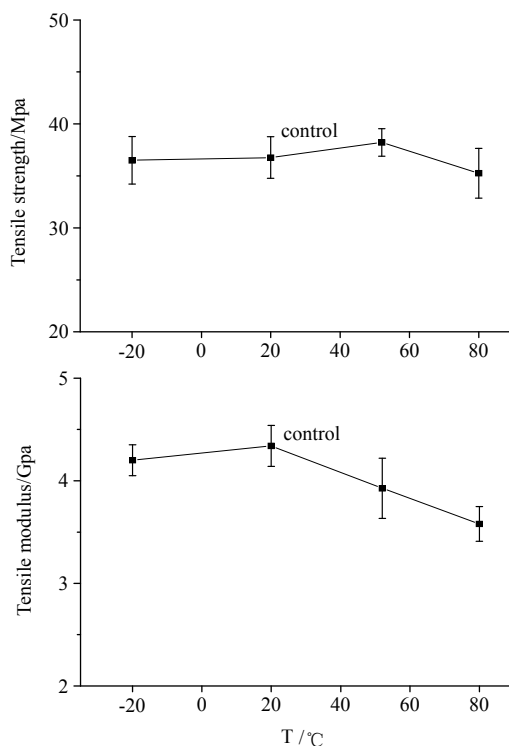


Fig. 5 Tensile properties of treated WPC by temperature

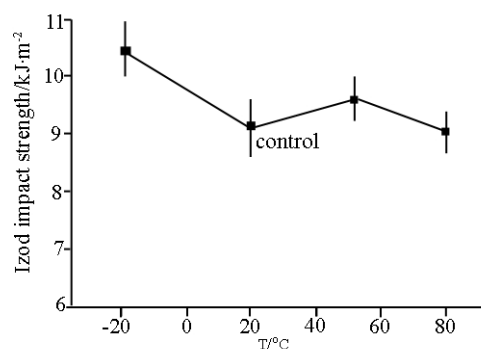


Fig. 6 Izod unnotched impact strength of treated WPC by temperature

X-ray diffraction (XRD)

Analysis of WPC using XRD showed both HDPE and wood diffraction peaks. Wood cell walls mainly consist of cellulose, hemicellulose, and lignin. Both the hemicellulose and lignin present amorphously; however, cellulose has both amorphous and crystalline regions that can result in diffraction peaks overlapping those of HDPE (Lei et al. 2007). The XRD patterns of treated composite samples in the 2θ range of the 18°C–26°C spectra are shown in Fig. 7. The peaks corresponding to the 110 and 200 lattice planes for HDPE are apparent and data are summarized in Table 1. Change of temperature did not cause a shift in peak position but peak intensity declined substantially at higher temperatures (Fig. 7). The values for the 110 lattice plane and 200 lattice plane declined gradually at increased treatment temperatures, which might be attributed to the cooling rate. This result also demonstrates that the crystallinity (X_c) of WPC can be reduced by thermal treatments. The reduction can be explained by reconfiguration of HDPE molecules.

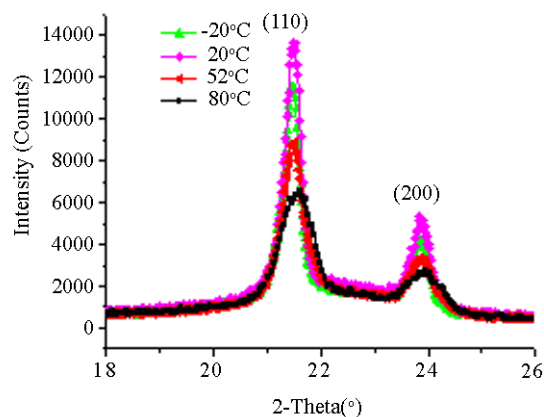


Fig. 7 X-ray diffractogram of WPC composite by temperature

Table 1. Summary of XRD data of WF-HDPE composite

Treating temperatures (°C)	Peak position		Half-height width		Crystalline thickness		Degree of crystallinity
	θ (°)		β_0 (°)		(nm)		X_c (%)
	(110)	(200)	(110)	(200)	(110)	(200)	-
-20	10.74	11.93	0.42	0.54	19.25	15.03	48.5
20	10.74	11.93	0.40	0.54	21.27	15.03	50.1
52	10.75	11.93	0.52	0.76	15.55	10.68	39.4
80	10.80	11.98	0.82	1.14	9.86	7.12	36.4

Conclusion

Treatment temperatures had a remarkable influence on the size of WPC, which initially expanded and then slowly contracted as temperatures rose. This phenomenon is important for installation of WPC. The dimensional change is assumed to be due to the reconfiguration of HDPE molecules and weight loss of WPC. Thermal treatment at 52°C and relative humidity of 50% for 16 days can improve the mechanical properties of WPC. The degree of crystallinity of WPC declined with increasing treatment temperature, which could explain the reduction of the modulus of WPC.

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